LUBRICITY OF JET FUELS

STATEMENT #2 UNCLASSIFIED

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AF Aero Propulsion Lab W-P, AFB, Ohio 45433

ESSO RESEARCH AND ENGINEERING COMPANY

LUBRICITY PROPERTIES
OF
HIGH-TEMPERATURE
JET FUELS

J.K. Appeldoorn

F.F. Tao

Esso Research and Engineering Co.

Products Research Division

Linden, New Jersey

QUARTERLY REPORT NO. 9

15 May - 15 August, 1967

CONTRACT NO. AF33 (615) 2828

FOR

Air Force Aero Propulsion Laboratory

Air Force Systems Command

Wright-Patterson Air Force Base, Ohio

TABLE OF CONTENTS

FOREWORD

This report was prepared by the Advanced Lubrication Project, Products Research Division, Esso Research and Engineering Company at Linden, New Jersey under Contract AF33 (615) 2828. This program is administered by the Air Force Aero Propulsion Laboratory, Air Force Systems Command with Arthur F. Levenstein, Capt., USAF as coordinator.

This report covers work conducted from 15 May to 15 August, 1967.

ABSTRACT

Scuffing, as distinct from wear, can be made to occur in the ball-on-cylinder device by going to 1000g load and 300F. It is evidenced by chattering during test and a pronounced wear track on the cylinder, easily visible with a surface roughness profile. Scuffing is more likely with highly-refined fuels and an atmosphere of wet air. Additives can inhibit scuffing but they differ in their effectiveness. Sulfur compounds have little or no effect at jet fuel concentrations.

Abrasive wear is shown to be an important wear mechanism in the Vickers vene pump test. This is believed to be triggered by corrosive wear, which forms the abrasive iron oxide.

Techniques have been worked out to obtain "bone-dry" conditions and measure accurately the water content. Scuffing of aromatics in argon tends to be inhibited by small amounts of water.

I. INTRODUCTION

Previous work on this contract has shown the importance of several variables. In particular:

- It has been found that aromatic hydrocarbons impart excellent lubricity to paraffinic fuels but no explanation has been found for their behavior Certain aromatics also tend to scuff very easily in dry, inert atmospheres.

- Dissolved oxygen prevents the scuffing of these aromatics but promotes corrosive wear of paraffins.

- Dissolved water has directionally the same effect as oxygen. It has not been investigated as fully, however.

- The effect of temperature is to promote wear and scuffing. This effect is often masked by the oxidation of the fuel to form polar compounds. Therefore, the effect of additives is difficult to assess at high temperatures.

The present report further confirms the effect of temperature, shows the importance of abrasive wear when wear debris are present, and presents a quantitative investigation of the effect of dissolved water.

II. EFFECT OF TEMPERATURE ON WEAR

A. Scuffing Wear

It was noted in previous ball-on-cylinder tests that scuffing was more severe at higher temperatures as evidenced by excessive friction and chattering. To investigate the temperature effect in the severe wear region, ball-on-cylinder tests were run at a load at which scuffing might occur at a certain high temperature. In order to avoid damage of the friction measuring device, the spring was blocked so that no friction reading was taken; severe or scuffing wear was recognized by the noise from chattering. Several interesting phenomena were observed from these tests: (1) When chattering occurred, an obvious scuffing track was observed on the cylinder. Scuffing wear was further confirmed by the Talysurf profile measurement. (2) For PW-523, a highly-refined fuel, scuffing occurred at a lower temperature in air than in argon. (3) A highly-refined fuel gave more scuffing wear than a currently marketed fuel. (4) Jet fuel additives showed their effectiveness in reducing scuffing, while sulfur compounds gave little effect.

1. PW-523 Gave More Scuffing Wear Than RAF-176-64

Ball-on-cylinder tests were made on PW-523, a highly-refined fuel, at 300F and various loads from 60 to 1000 grams within which no scuffing was observed in tests at room temperature as reported previously. The results are shown in Table 1. At 1000g load in air, scuffing was quite evident as noted by chattering during the tests and an abrupt increase of wear as shown in Figure 1. In argon, the runs at all the loads were quiet and the wear increased slightly at higher loads. It appears that the severe wear in air was corrosive wear or was initiated by corrosive wear.

Ball-on-cylinder tests were therefore made at the more severe conditions (1000g load and various temperatures from 160F to 300F) to compare PW-523 and RAF-176-64, a currently marketed fuel known to have better lubricity. The results are shown in Table 2. PW-523 gave scuffing (chattering during the run) at all temperatures in air, while RAF-176-64 did not give any chattering even at 300F. In argon, no scuffing was noted for either fuel. The difference in performance of these two fuels in air is clearly seen in Figure 2.

When chattering occurred during the run, an obvious scuffing wear track was noted on the cylinder. The wear on the cylinder was examined by Talysurf profile measurements. Figure 3 is a typical example of these measurements which show the difference of wear on the cylinder for PW-523 and RAF-176-64. This is an even clearer demonstration of the difference in antiscuffing ability for these two fuels in various atmospheres. The approximate wear volume (V) on the cylinder was computed from the depth (s) and the width (W) of the wear track and the radius of the cylinder (R), assuming its cross section to be a circular segment:

$$V = 2/3\ Ws \cdot 2\pi R = 4/3\pi RWs$$
$$= 93\ Ws$$

The computed wear volume on the cylinder for these runs showing severe wear is also presented in Table 2. It is in the order of magnitude of 1 mm^3. The wear volume on the ball can be computed from the wear scar diameter (d) and the radius of the ball (r) and is ($\pi d^4/64r$) approximately. For a half-inch ball with a wear scar

TABLE 1

EFFECT OF LOAD ON WEAR AT 300F

(Ball-on-Cylinder Tests, 240 rpm, 32 min, Steel-on-Steel)

Fuel: PW-523

Load, g	Wear Scar Diameter, mm Dry Argon	Dry Air	Wet Air
60	0.22	0.36	0.42
120	0.27	0.52	0.62
240	0.32	0.50	0.65
480	0.37	0.53	0.77
1000	0.35 (0.31)	0.98* (1.01*)	1.08* (1.05*)

* Chattering occurred.

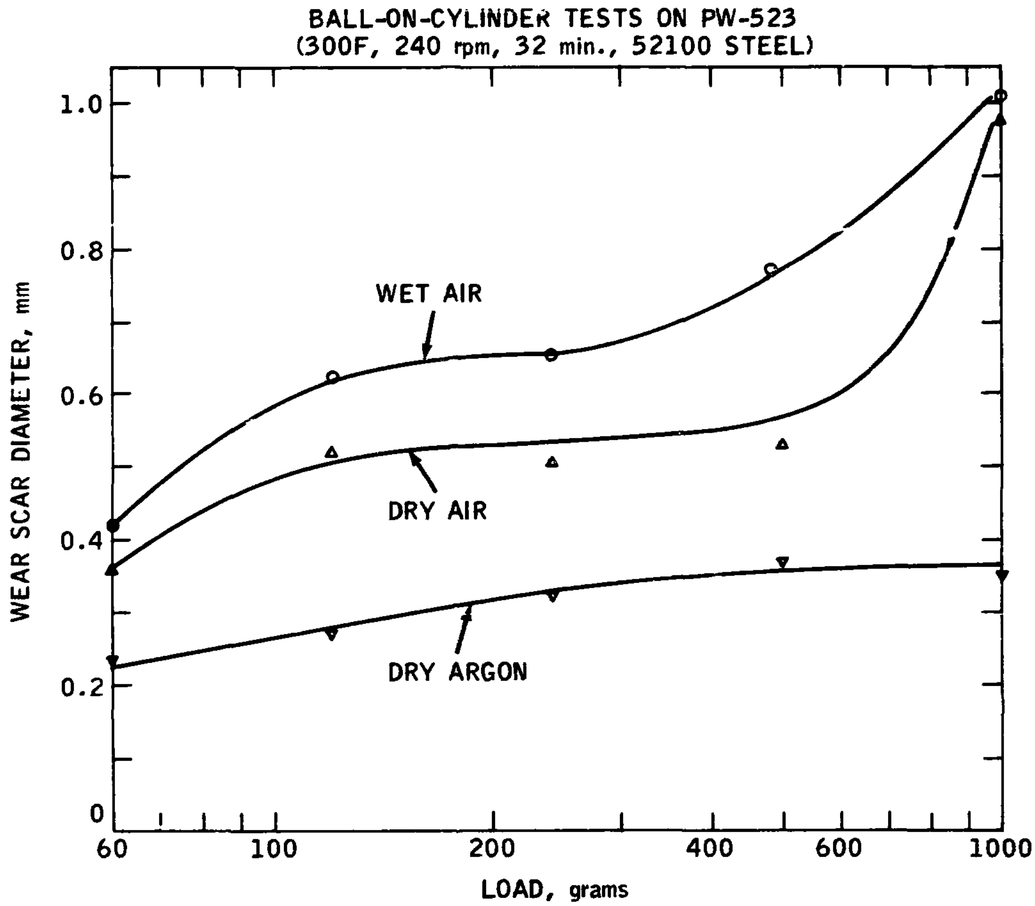


FIGURE 1 - HIGH TEMPERATURES CAUSE INCREASED SCUFFING

TABLE 2

EFFECT OF TEMPERATURE ON WEAR

(Ball-on-Cylinder Tests, 1000g, 240 rpm, 32 min, Steel-on-Steel)

		Dry Argon		Dry Air		Wet Air	
Fuel	Temp., °F	Wear Severity	WSD, mm	Wear Severity	WSD, mm	Wear Severity	WSD, mm
PW-523	160	Mild	0.28	Severe* (1.2)	1.05	Severe* (1.7)	1.09
	240	Mild	0.28	Severe* (2.2)	1.17	Severe* (2.6)	1.22
	300	Mild	0.31 (0.35)**	Severe* (1.3)	1.01 (0.98)**	Severe* (1.2)	1.05 (1.08)**
RAF-176-64	160	Mild	0.30	Mild	0.39	Mild	0.48
	240	Mild	0.42	Mild	0.41	Mild	0.57
	300	Mild	0.35 (1.02)** (0.38)** (0.45)**	Mild	0.51 (0.43)**	Mild	0.55 (0.93)**

---

* Chattering during run and very obvious scuffing marks on the cylinder. Data in parentheses are computed wear volume in mm^3 on the cylinder based on Talysurf profile measurements.

** Data on repeated runs.

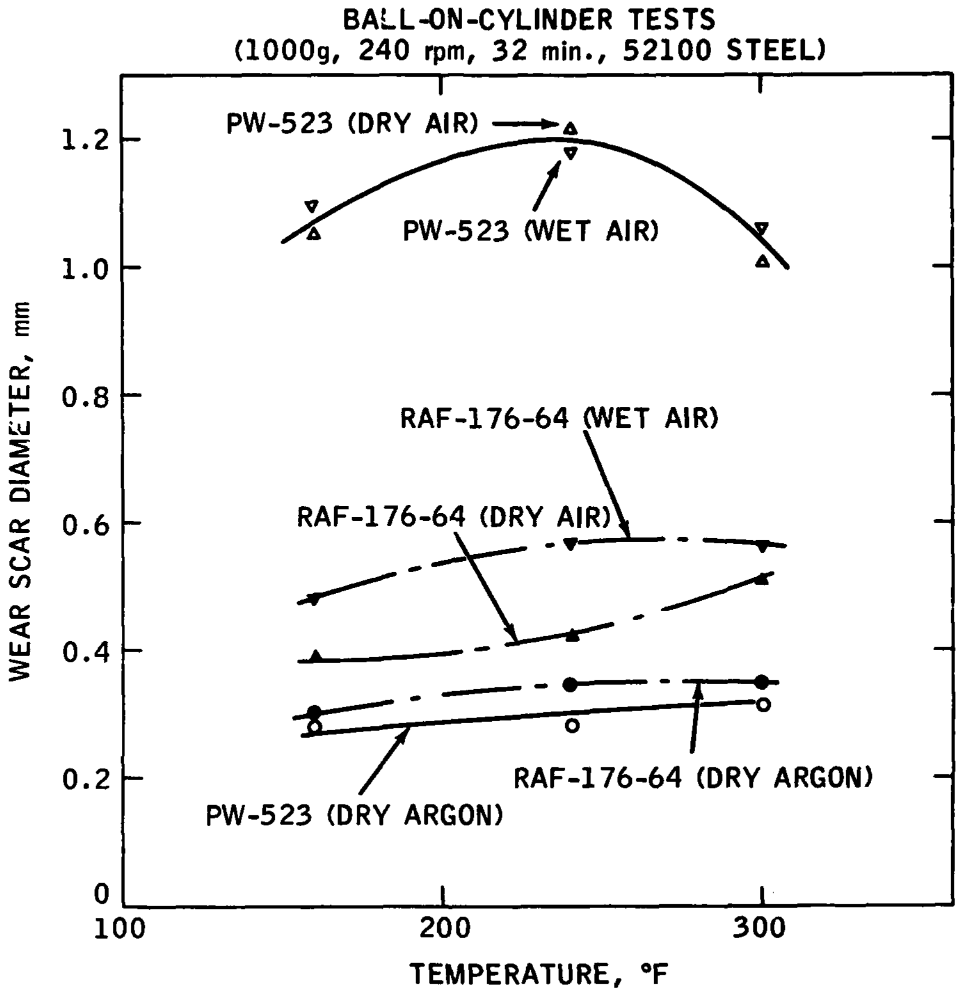
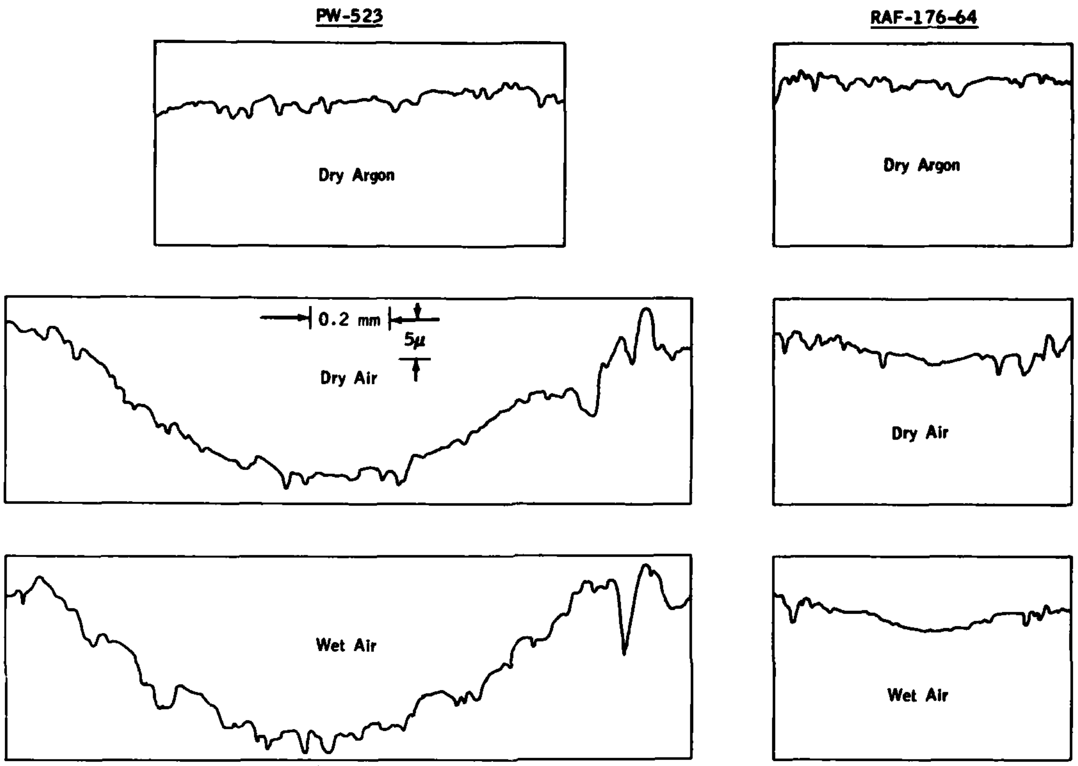


FIGURE 2 - PERFORMANCE OF TWO DIFFERENT FUELS IN AIR ATMOSPHERE



BALL-ON-CYLINDER TESTS (1000g, 240 rpm, 240F, 32 min., 52100 STEEL)

FIGURE 3 - TALYSURF PROFILE OF WEAR TRACK ON CYLINDER UNDER SCUFFING AND NON-SCUFFING CONDITIONS

(Ball-on-Cylinder Tests: 1000g, 240 rpm, 240F, 32 min, 52100 Steel)

diameter of 1 mm, its wear volume is about 0.01 mm^3. This indicates that the wear was much more on the cylinder than on the ball once severe wear occurred. Since the cylinder is softer than the ball (35 R_c vs 60 R_c), it is reasonable that the scuffing wear should be much more pronounced on the softer surface.

2. Jet Fuel Additives Show Antiscuffing Effect

The effectiveness of one EP additive, ZnDDP, and two jet fuel additives, ER-1 and ER-3, were evaluated at a concentration of 50 ppm in ball-on-cylinder tests. The conditions (1000g load and temperature 160-300F) were such that the base fuel, FW-523, would give severe wear. It will be seen (from Table 3) that ER-3 prevented scuffing (chattering) at all temperatures, ER-1 at 160F and 240F but not 300F, and ZnDDP only at 160F. Essentially, the same results were obtained in both dry air and wet air.

An important observation is that high wear on the ball is not always accompanied by high wear on the cylinder. Figures 4 and 5 plot both ball wear and cylinder wear for these runs. Note that at 160F, all additives gave zero cylinder wear (no scuffing), but the ball wear varied from 0.53 to 0.97. On the other hand, high wear on the cylinder is invariably accompanied by high wear on the ball. In other words, when scuffing occurs wear is high on both surfaces, but when scuffing does not occur only the ball shows measurable wear. By examining both surfaces, it is possible to determine whether high wear on the ball is due to scuffing or to normal corrosive wear.

3. A Disulfide Showed Slight Antiscuffing Effect

Three organic sulfur compounds, thiophenol (a mercaptan), dioctyl sulfide (a sulfide) and dibenzyl disulfide (a disulfide), were tested in ball-on-cylinder tests at 1000g load using FW-523 as the base fuel. The concentration for thiophenol was 30 ppm S which is above the allowable limit (10 ppm) for mercaptan sulfur in jet fuels. The concentration for sulfides was 100 ppm S, the sulfur content of most jet fuels. Both thiophenol and dioctyl sulfide did not show any antiwear and antiscuffing effect as shown in Table 4. The disulfide showed some antiscuffing effect in that the runs at 160F (but not 240F) ran without any chattering noise and no severe wear was measured on the cylinder. However, the difference of wear scar diameters was not significant. It will require additional tests to decide whether the decrease in scuffing is due to the disulfide part of the molecule or just to the aromatic part.

4. The Scuffing Phenomenon for Polynuclear Aromatics in Argon Was Further Confirmed at a Higher Temperature

It was previously reported that condensed ring aromatics, unlike paraffinic fuels, gave much higher wear in argon than in air. For the purpose of investigating this phenomenon at a higher temperature, ball-on-cylinder tests were made on naphthalene, 1-methylnaphthalene and 2-methylnaphthalene at 300F and 1000g load in dry argon, wet argon and wet air. The order of wear severity in various atmospheres, as shown in Table 5, was the same as at room temperature, although the severity of wear increased at a higher temperature. The scuffing wear in argon is clearly shown in Figure 6, which is a typical example of Talysurf profiles on the cylinder for test runs for 2-methylnaphthalene. The effectiveness of the dissolved water and oxygen in preventing scuffing wear is clearly demonstrated in Figure 6.

TABLE 3

ANTISCUFFING EFFECT OF ADDITIVES

(Ball-on-Cylinder Tests, 1000g, 240 rpm, 32 min, 52100 Steel)

Additive in PW-523	Temp., °F	Dry Air Wear Severity	Dry Air WSD, mm	Wet Air Wear Severity	Wet Air WSD, mm
None	160	Severe	1.05	Severe	1.09
	240	Severe	0.87	Severe	1.17
	300	Severe	0.93	Severe	1.10
50 ppm ZnDDP	160	Mild	0.85	Mild	0.70
	240	Severe	0.91	Severe	1.00
	300	Severe	1.14	Severe	1.17
50 ppm ER-1	160	Mild	0.80	Mild	0.95
	240	Mild	0.70	Mild	0.85
	300	Mild*	1.13	Severe	1.07
50 ppm ER-3	160	Mild	0.53	Mild	0.70
	240	Mild	0.45	Mild	0.56
	300	Mild	0.55	Mild	0.53
		(Mild)**	(0.54)	(Mild)**	(0.56)

* Chattering at start for a short time; slight wear on the cylinder.

** Repeated runs.

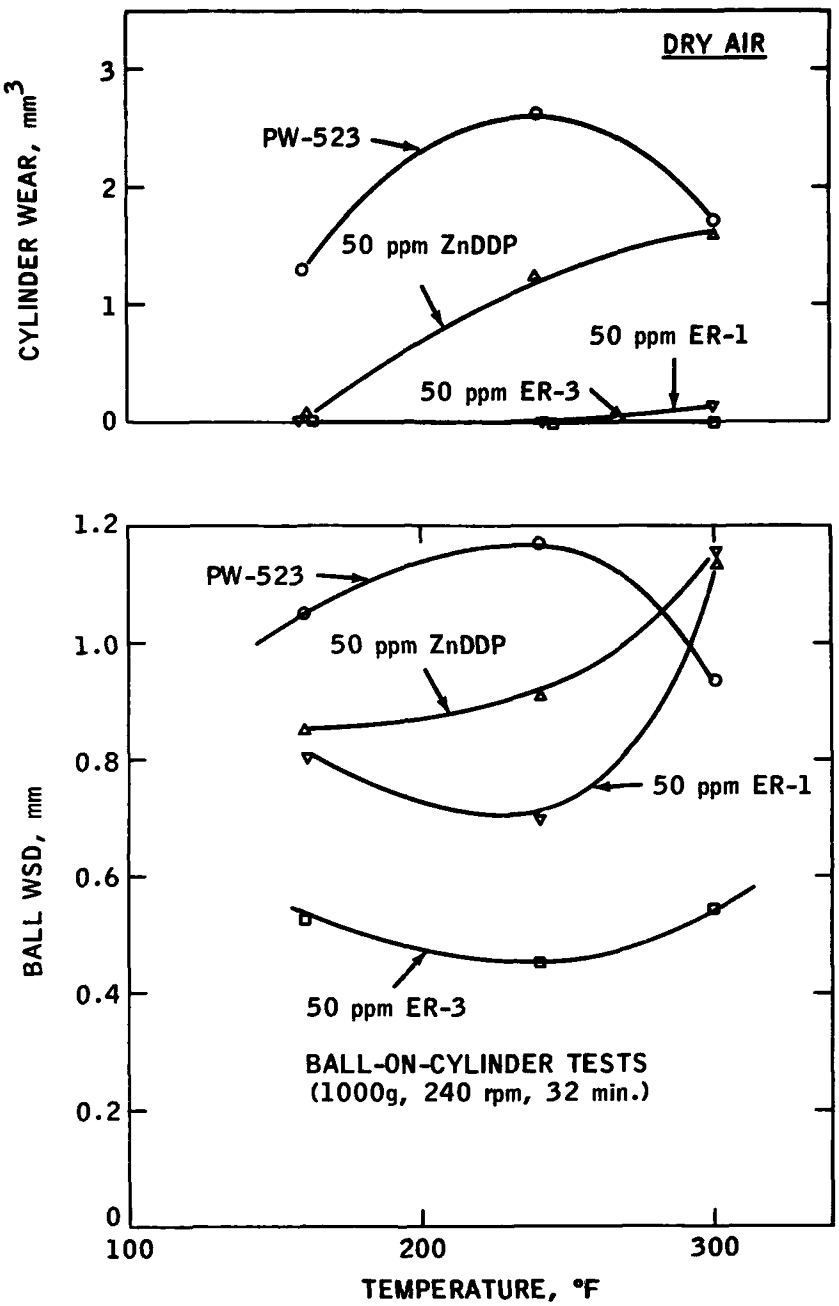


FIGURE 4 - COMPARISON OF BALL WEAR VS CYLINDER WEAR FOR ADDITIVE BLENDS IN DRY AIR

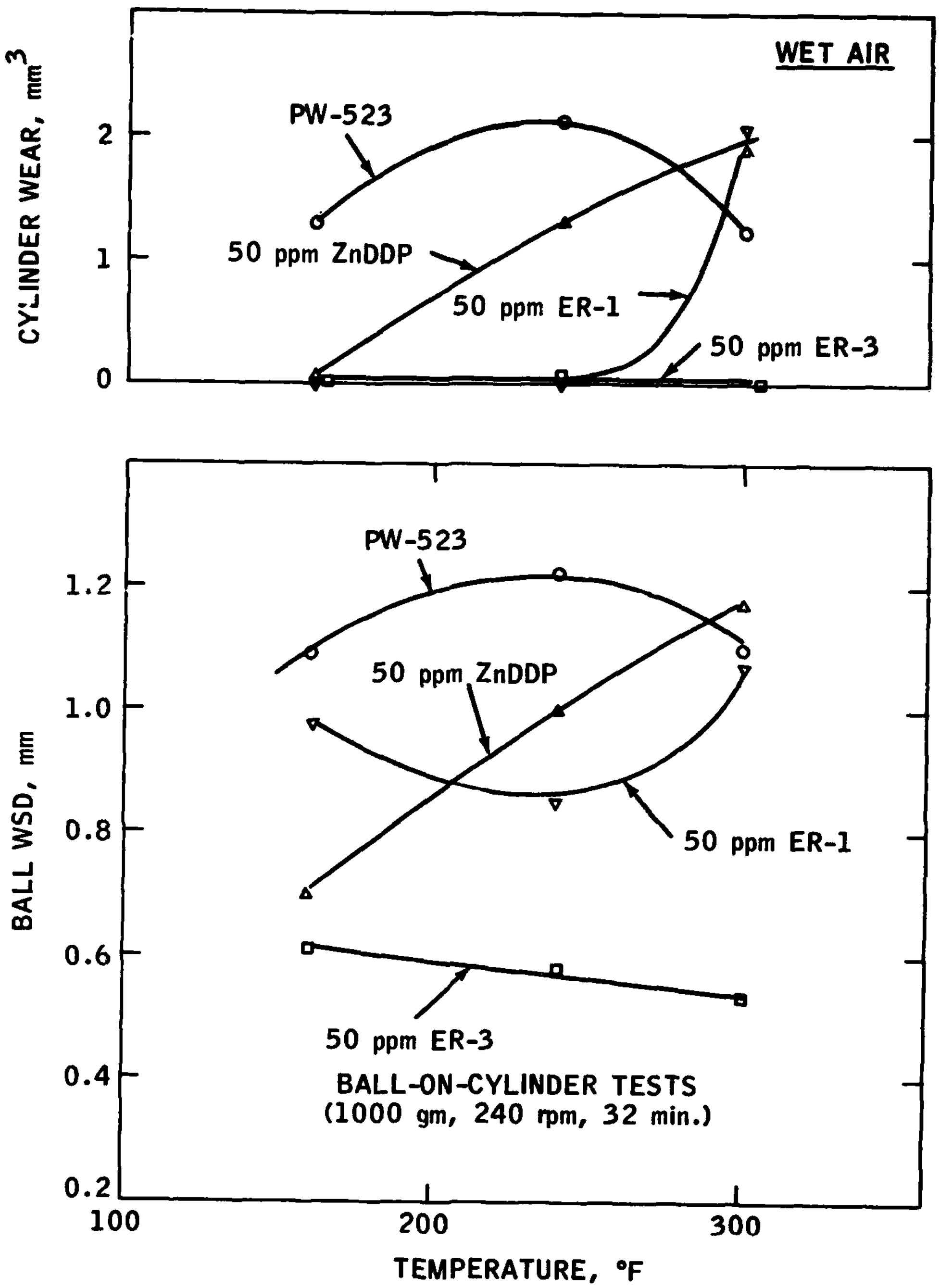


FIGURE 5 - COMPARISON OF BALL WEAR VS CYLINDER WEAR FOR ADDITIVE BLENDS IN WET AIR

TABLE 4

EFFECT OF SULFUR COMPOUNDS ON SCUFFING

(Ball-on-Cylinder Tests, 1000g, 240 rpm, 32 min, 52100 Steel)

Base Fuel: FW-523

Additive	Temp. °F	Dry Argon Wear Severity	Dry Argon WSD, mm	Dry Air Wear Severity	Dry Air WSD, mm	Wet Air Wear Severity	Wet Air WSD, mm
None	160	Mild	0.28	Severe* (1.2)	1.05	Severe* (1.7)	1.09
	240	Mild	0.28	Severe* (2.2)	1.09	Severe* (2.6)	1.17
50 ppm S as Thiophenol	160	Mild	0.42	Severe* (0.64)	0.92	Severe* (0.9)	0.94
	240	Mild	0.41	Severe* (1.05)	1.10	Severe* (1.7)	1.20
100 ppm S as Dioctyl Sulfide	160	Mild	0.28	Severe* (0.97)	1.06	Severe* (1.7)	1.14
	240	Mild	0.35	Severe* (1.6)	1.14	Severe* (2.3)	1.22
100 ppm S as Dibenzyl Disulfide	160	Mild	0.39	Mild	0.86	Mild (0.07)	0.92
	240	Mild	0.28	Severe* (1.3)	1.05	Severe* (1.6)	1.02

* Chattering during runs and very obvious scuffing marks on the cylinder. Data in parentheses are computed wear volume in mm^3 on the cylinder based on the Talysurf profile measurements.

TABLE 5

WEAR OF BINUCLEAR AROMATICS AT 300F

(Ball-on-Cylinder Tests, 1000g, 240 rpm, 32 min, 52100 Steel)

Aromatics	Dry Argon Wear Severity	Dry Argon WSD, mm	Wet Argon Wear Severity	Wet Argon WSD, mm	Wet Air Wear Severity	Wet Air WSD, mm
Naphthalene	Severe* (8.1)	1.45	--	--	Mild	0.69
1-Methylnaphthalene	Severe* (5.0)	1.87	Mild	0.61	Mild	0.48
2-Methylnaphthalene	Severe* (8.1)	1.44	Mild	0.92	Mild	0.45

* Chattering during runs and very obvious scuffing marks on the cylinder. Data in parentheses are computed wear volume in mm^3 on the cylinder based on Talysurf profile measurements.

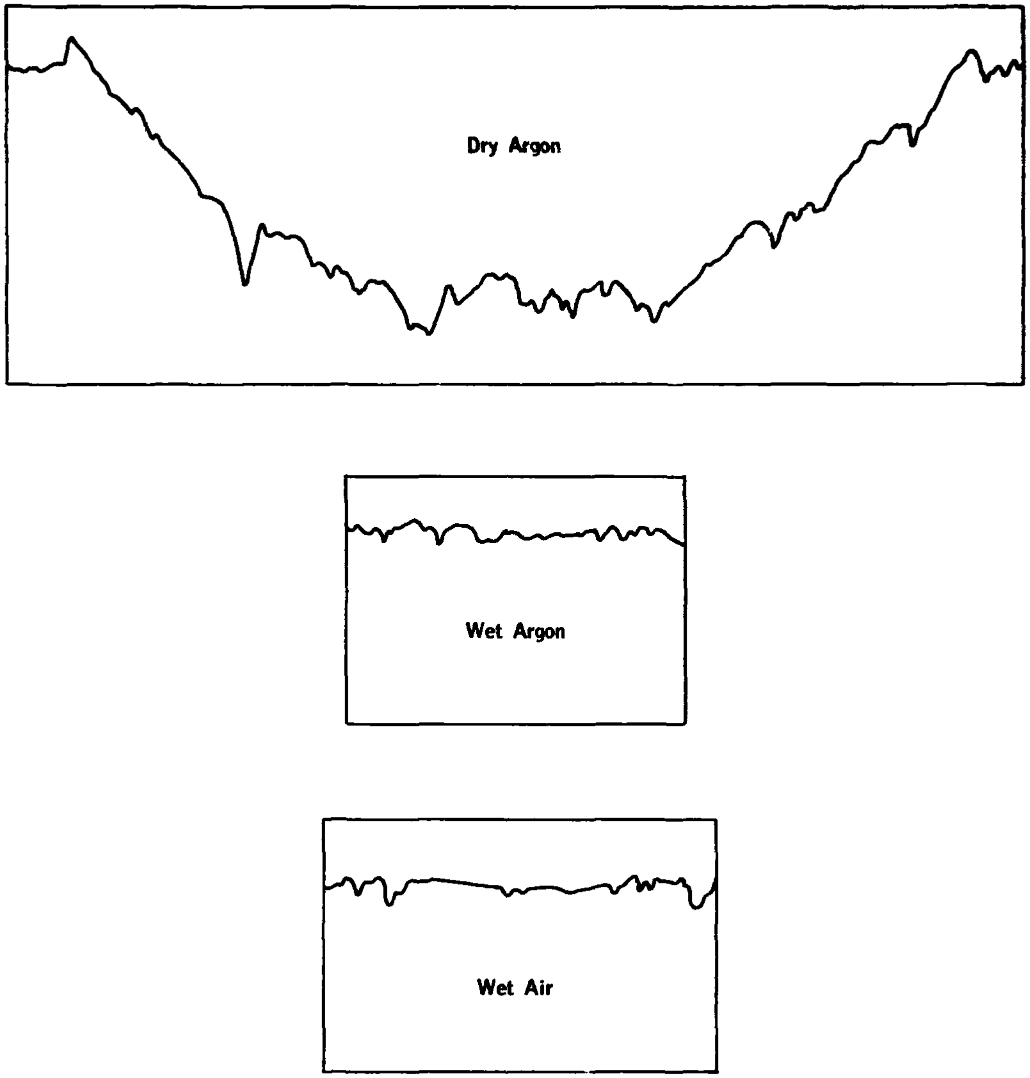


FIGURE 6 - TALYSURF PROFILE OF 2-METHYLNAPHTHALENE IN BALL-ON-CYLINDER TESTS
(1000g, 240 rpm, 300F, 32 min, 52100 Steel)

5. Effect of Oxidation on Wear is Confirmed

As reported previously, the oxidation of a fuel during test could mask the temperature effect so that the wear is lower at 300F provided the load is low and no scuffing occurs. To study the effect of oxidation on wear for different hydrocarbons, ball-on-cylinder tests were made on dodecane (alkane), dodecene (olefin), and indene (aromatic) at 240g load. These hydrocarbons were redistilled chemical reagents; the dodecane was further purified by passing through the silica gel column before the test. A series of tests was carried out on each hydrocarbon in the following sequence: (1) a ball-on-cylinder test in argon or air at 77F, (2) heat to 300F in argon, (3) a ball-on-cylinder test on the same sample in argon or air at 300F, (4) cool to 77F in argon, and (5) a repeat ball-on-cylinder test at 77F in argon or air. The results are shown in Table 6.

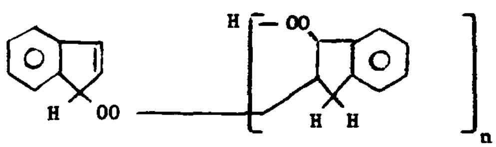
In air, dodecane gave higher wear at 77F than at 300F. This clearly indicates the oxidation effect as evidenced by the lower wear in the repeat run at 77F and the increase of Neut. No. in the sample after tests. In argon, indene gave high wear at 77F and caused scuffing at 300F--in a nonoxidizing atmosphere the wear became more severe at a higher temperature. It is also noteworthy that the oxidation of indene at 300F did not change its poor lubricity as shown in the repeat run at 77F.

It is well-known that there are two possible ways for the propagation of the alkyl peroxy radical in autoxidation of hydrocarbons, namely.

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (1)$$

$$ROO\cdot + C{=}C \longrightarrow ROOC - C\cdot \qquad (2)$$

For dodecane, Reaction (1) is the only possible step, and the product of the oxidation is mainly carbonyls such as a carboxylic acid that may adsorb on the surface to form a protective film. For indene, the propagating step has been found mainly to be Reaction (2), and the major product after oxidation is a copolymer with the oxygen. (Refer to Russell, G. A., J. Am. Chem. Soc., 78, 1035 (1956)). The oxy-polymer has been found to be:



This polymeric film may be formed in the contact region to give wear protection in the presence of oxygen. However, this does not explain why indene has such poor antiscuffing properties in the first place.

B. Pump Wear

Vickers vane pump tests were made at 300F to investigate pump performance at high temperatures. Wear debris was obtained from pump tests in dry air and wet air. The chemical analyses and microscopic examinations of wear debris from these shed some light on the wear phenomena in the pump.

TABLE 6

EFFECT OF OXIDATION ON FRICTION AND WEAR

Sequence of Test	Dodecane		Dodecene		Indene	
	CoFr	WSD, mm	CoFr	WSD, mm	CoFr	WSD, mm
1. 77F, Argon	0.16	0.28	--	0.28	0.15	0.85
Air	--	0.67	--	0.30	0.13	0.35
2. 300F, Argon	0.14	0.30	0.11	0.35	**	0.87*
Air	0.22	0.38	0.14	0.32	0.22**	0.38
3. 77F, Argon	0.17	0.33	0.12	0.29	0.18**	0.80
Air	0.17	0.35	0.11	0.29	0.17	0.33
Final Neut No, ppm KOH	162		276		83	

* Test stopped at 4 minutes due to excessive friction and chattering.

** Friction reading erratic.

1. Oxidation of Fuel Masked the Temperature Effect at 300F

Vickers vane pump tests on Bayol 35 at 300F are compared in Table 7 with those at 240F previously reported. The severity of these tests is believed to be similar. At 300F, the viscosity was lower and the pressure, equivalent to load, was proportionally lower. In nitrogen, the wear was slightly higher at 300F than at 240F. This represents the temperature effect. In wet air, the wear at 300F was very low, indicating that the effect of oxidation of the fuel masked the temperature effect.

It is believed that the load on the rubbing surfaces in the pump is not high enough to cause scuffing and that the wear is primarily corrosive wear, or is abrasive wear caused by the iron oxide particles resulting from corrosive wear. Supporting evidence of non-scuffing in the pump was obtained from pump tests on 1-methylnaphthalene in argon. Since it was found in ball-on-cylinder tests that 1-methylnaphthalene gave scuffing in argon at relatively low loads, the very low wear in the pump tests, as shown in Table 8, indicates that the load on the rubbing surface in the pump is not severe enough to cause scuffing.

2. Chemical Analyses of Wear Debris Showed Evidences of Abrasive Wear Due to Oxides

Vickers vane pump tests at 90F and 350 psig were made on Bayol 35 in dry air and wet air. The wear particles were so fine that they could pass through the 20 μ filter in the circulating system. The fuel after tests was filtered through a 5 μ Millipore filter, washed with hexane, and dried. Microscopic examinations were made on these samples before and after filtration.

The results with optical microscopic examination is briefly summarized as follows: Some particles are black and do not transmit light. Others are semi-transparent and of an orange to brownish color, indicating the presence of Fe_2O_3 and/or $Fe(OH)_3$. These appear to be aggregates of small particles. Some agglomerates are combinations of black and brown particles. The opaqueness of the particles makes it difficult to determine, with any certainty, if crystallinity exists. A sample was examined by X-ray diffraction. Only α-Fe could be definitely identified. The particles vary in size from an occasional large one, about 30 μ in its longest dimension, to ones as small as 2 μ. Even the smallest appear to be agglomerates. The particle size that accounts for the bulk of the material is estimated in the 10-15 μ range.

Electron microscopic examinations were also made on Bayol 35 before and after pump tests and the filtrate from the Millipore filter. The micrographs are shown in Figures 7-9. The filtrate, although appearing clean by visual observation, still contained a considerable amount of very fine particles of <2 μ size. In view of very fine wear particles, it seems that the severe wear in the vane pump is not attributed to the metal adhesion but rather to abrasive wear.

Chemical analyses were made on these wear debris. The iron of various valence states was analyzed by an unpublished procedure developed by Esso Research. The oxygen was analyzed by neutron activation. The carbon and hydrogen analyses were by the IKA Microcombustion method. The results, as shown in Table 9, indicate about 30% of Fe-oxides in the wear debris. Since the oxygen content is more than that needed to form FeO and Fe_2O_3, it is believed that iron hydroxide may also be present. The composition of oxides, as shown in Table 10, was estimated by solving

TABLE 7

VICKERS VANE PUMP PERFORMANCE OF BAYOL 35 AT HIGH TEMPERATURES

	Dry Nitrogen (24 Hr. Runs)		Wet Air (4 Hr. Runs)	
Sump Temperature, °F	240	300	240	300
Pressure, psig	150	125	150	125
Viscosity, cp at sump temperature	0.60	0.43	0.60	0.43
Pumping Rate, gpm	0.49	0.37	0.27	0.38
Volume Efficiency, %	27	21	15	21
Wear, mg				
Wt. Loss of Vanes	1	11	22	2
Wt. Loss of Ring	23	144	473	19
Surface Roughness, μ inch				
Vanes, Initial	20	5	11	11
Vanes, Final	31	77	>200	12
Rings, Initial	12	11	27	11
Rings, Final	7	41	>200	7

TABLE 8

VICKERS VANE PUMP TESTS ON 1-METHYLNAPHTHALENE IN NITROGEN

Pressure, psig	400	370
Pumping Rate, gpm	0.39	1.07
Volume Efficiency, %	22	59
Wear, mg		
Wt. Loss of Vanes	1	1
Wt. Loss of Ring	0	2
Surface Roughness, μ inch		
Vanes, Initial	8	7
Vanes, Final	9	7
Ring, Initial	15	11
Ring, Final	14	11

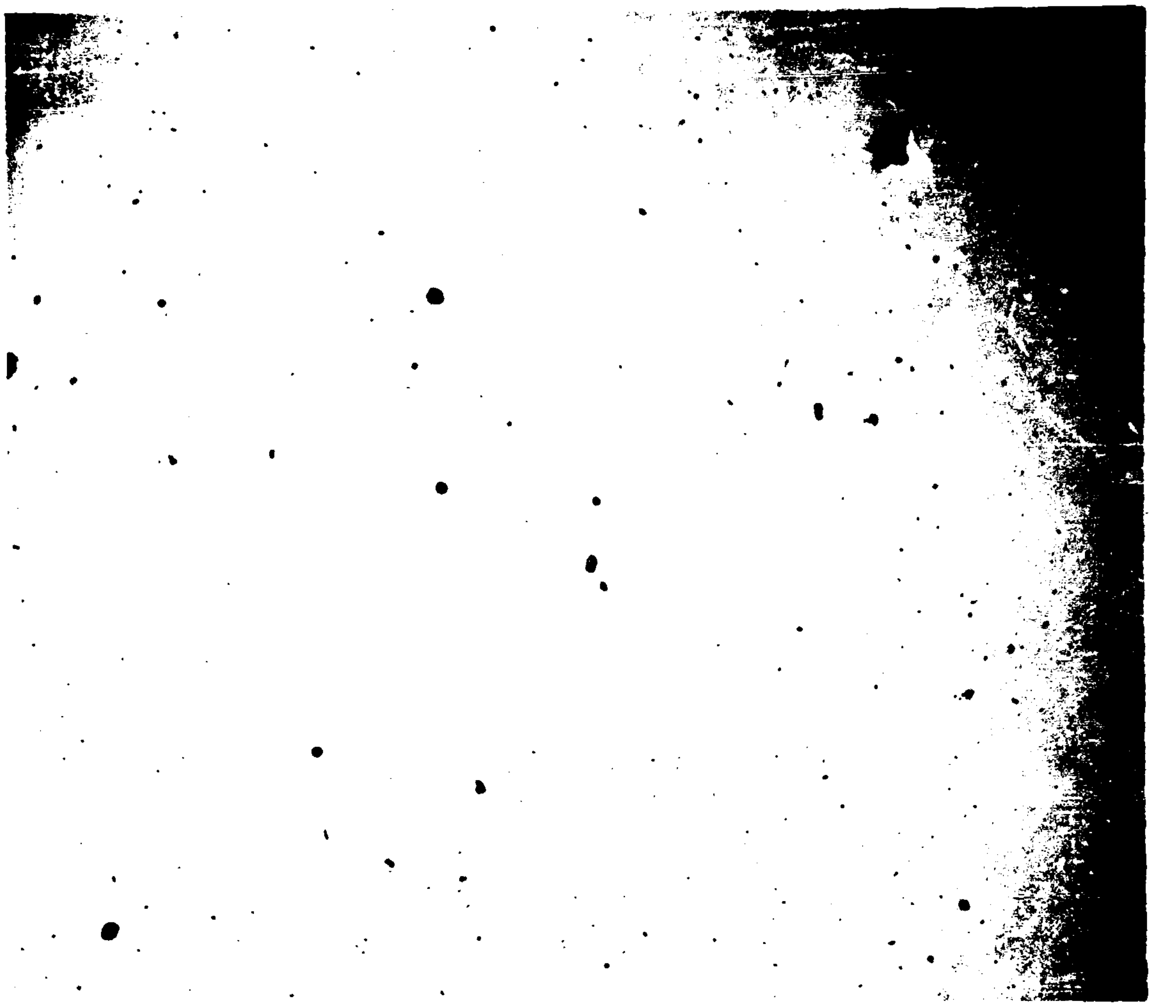


FIGURE 7 - ELECTRON MICROGRAPH OF BAYOL 35--7000X

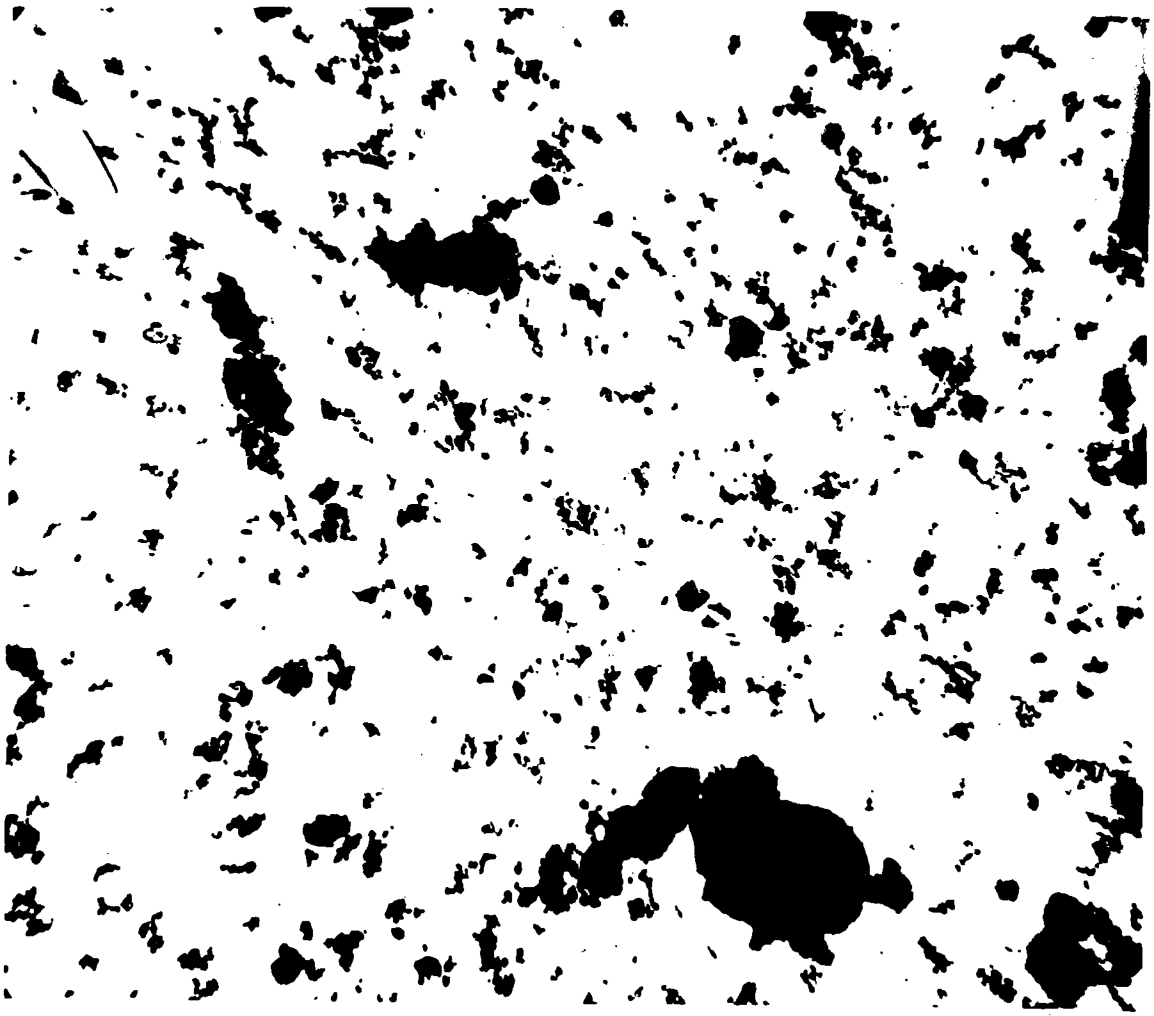


FIGURE 8 - ELECTRON MICROGRAPH OF BAYOL 35 AFTER A PUMP TEST AT 350 PSIG IN WET AIR--7000X

FIGURE 9 - MICROGRAPH OF FILTRATE FROM 5 μ MILLIPORE FILTER FOR BAYOL 35 AFTER PUMP TEST--7000X

TABLE 9

ANALYSES OF WEAR DEBRIS FROM PUMP TESTS

Analyzed Items	Sample From a Pump Test at 350 psig, 90F in Wet Air		Sample From a Pump Test at 350 psig, 90F in Dry Air	
Fe^{0}	59.1		71.0	
Fe^{+2}	9.0	80.0	7.8	85.9
Fe^{+3}	11.9		7.1	
Total Fe (By Analysis)	80.4		84.8	
Oxygen	10.5		6.1	
C	7.0		7.0	
H	0.2		0.1	

TABLE 10

ESTIMATED COMPOSITION OF IRON OXIDE IN WEAR DEBRIS

In Wet Air	Percent	Percent: Fe^{+2}	Fe^{+3}	O	H
1. Assumed to Contain $Fe(OH)_3$:					
FeO	11.6	9.0	--	2.6	--
Fe_2O_3	7.6	--	5.3	2.3	--
$Fe(OH)_3$	12.6	--	6.6	5.7	0.3
	32.0	9.0	11.9	10.6	0.3
2. Assumed to Contain $Fe(OH)_2$:					
FeO	0	--	--	--	--
Fe_2O_3	17	--	11.9	5.1	--
$Fe(OH)_2$	15.2	9.4	--	4.6	0.3
	32.2	9.4	11.9	9.7	0.3
In Dry Air					
1. Assumed to Contain $Fe(OH)_3$:					
FeO	10	7.8	--	2.2	--
Fe_2O_3	6.9	--	4.9	2.0	--
$Fe(OH)_3$	4.1	--	2.1	1.9	0.1
	21.0	7.8	7.0	6.1	0.1
2. Assumed to Contain $Fe(OH)_2$:					
FeO	6.5	5.0	--	1.5	--
Fe_2O_3	10.1	--	7.0	3.1	--
$Fe(OH)_2$	4.6	2.9	--	1.6	0.1
	21.2	7.9	7.0	6.1	0.1

three simultaneous equations which were formulated by the Fe^{+3}, Fe^{+2} and O_2 balances and assuming the iron hydroxide to be either $Fe(OH)_3$ or $Fe(OH)_2$. The computed % H agrees well with the analytical results. The Fe-distribution in wear debris, assuming it contains $Fe(OH)_3$, is summarized below:

	In Wet Air		In Dry Air	
	% By Weight	% Distribution	% By Weight	% Distribution
Fe	59.1	65.0	71.1	77.1
FeO	11.6	12.7	10.0	10.9
Fe_2O_3	7.6	8.4	6.9	7.5
$Fe(OH)_3$	12.6	13.9	4.1	4.5
	90.9	100.0	92.1	100.0

It will be seen that oxidation is greater in wet air than in dry air and that particularly the amount of iron hydroxide is greater. It is also noteworthy that the majority of the wear is as unoxidized iron, the ratio of iron to iron oxides being 2-3 to 1, indicating the importance of abrasive wear when iron oxide particles are present. This abrasive wear is clearly triggered by corrosive wear, since it does not occur under an inert blanket.

The high carbon content in the wear debris is surprising in that the steel contains only about 1% C. More analyses are being made to identify whether it is elemental carbon, carbide, or adsorbed oil that was not removed by the hexane wash.

III. EFFECT OF DISSOLVED WATER ON WEAR

Previous work had shown the importance of water content on wear and scuffing. The driest condition obtained experimentally was 20-30 ppm water, which was the humidity of the argon or air as received in compressed gas cylinders. It was felt that even this small quantity of water could have some effect, so a program was carried out under "bone-dry" conditions--<1 ppm water in the atmosphere.

The bone-dry conditions were obtained using a heatless dryer developed at Esso Research by C. W. Skarstrom. The dryer consists of two columns of desiccant (silica gel) used alternately. Compressed gas (30-150 psi) passes through one column where its moisture is completely removed. A small part of this dried gas is then expanded and passed through the second column. Because the drying efficiency depends on the volume of gas used and not its weight, this expanded gas regenerates the silica gel to its previous condition. A timer switches the gas from one column to the other every 30 seconds, so that one column is working while the other is regenerating. Thus, complete dryness is obtained without heating and without using cryogenic temperatures. The gas leaves the drier at less than 1 ppm water. This amounts to >95% water removal from an already very dry gas.

A gas-mixing system was constructed so that any desired mixture of oxygen and nitrogen could be obtained, and at any desired moisture level. Oxygen was analyzed in the gas phase by a Beckman Oxygen Analyzer. Water was analyzed in the gas phase by a Gilbarco Sorption Hygrometer. This instrument was satisfactory at very low water contents (<10 ppm); higher water content was determined from the mixing volumes of dry and moist gas.

The water content in the fuel (liquid phase) should follow Henry's Law, and therefore be calculable knowing the partial pressure of water in the surrounding atmosphere and the saturation content of water in the hydrocarbon.

For the friction and wear tests, the ball-on-cylinder machine was again utilized in this study. The sample cell was sealed to eliminate back diffusion from the atmosphere provided the sample gas flow rate was high enough. AISI 52100 steel balls and cylinders were used for most of the runs. The balls were initially of Rockwell Hardness 63 R_c. Some were heat-treated to give a hardness of 26 R_c. The cylinders are ~30 R_c. For several runs a Timkin roller bearing race of ~60 R_c hardness was utilized. This was not only harder but also rougher (30 μ" CLA vs 12 μ" CLA for the regular cylinder) so that differences observed could be caused by either the hardness or the roughness or both.

1. Dodecane Showed No Scuffing Even at Bone-Dry Conditions

To measure the dissolved water directly, some preliminary work was done with a new water analyzer developed by W. H. King of the Analytical Research Division of Esso Research. It consists of a gas chromatograph coupled to a crystal hygrometer. This work showed that serious errors exist in the literature on the solubility of water in hydrocarbons and that the Karl Fischer method is not dependable in many cases. It appears that the new technique is exceptionally well suited to jet fuels. But it was felt that a full-scale investigation of water solubilities, the speed at which dissolved water will equilibrate with the atmosphere, and the perturbing effect of surfactants, was beyond the scope of this contract.

For dodecane, the softened steel balls were used in hopes of accentuating corrosive wear. However, this did not occur. At bone-dry conditions wear was constant at oxygen concentrations below 2%. Above 2% oxygen, wear increased steadily but reached a plateau at 21% oxygen. Further increases in oxygen to 100% showed no increase in wear. Data are shown in the solid line on Figure 10. This is the usual corrosive wear phenomenon observed before.

Of greater interest is that no scuffing occurred under conditions of low-oxygen, low-water. There had been some feeling that the complete absence of adsorbed water would lead to scuffing.

A few tests were carried out using the hard (63 R_c) balls. These data are shown as the dashed line in Figure 10. The points agree closely with the soft-ball data giving low wear at low oxygen concentrations and increasing wear at higher concentrations. A discrepancy was at 100% oxygen, where wear was very high with the hard ball.

Also plotted on Figure 10 are two points in saturated air. The upper point (■) is with a softened ball; wear is much higher than in dry air. The lower point (▲) is with a hard ball; wear is only slightly higher than under dry conditions. This situation is somewhat anomalous: tests with the hard ball are more sensitive to dissolved oxygen than to dissolved water; tests with the softened ball are the reverse. Somewhat the same situation has been noted in comparing chrome steel to stainless steel. No explanation is readily apparent.

Some further tests were carried out using the harder Timkin bearing in place of the normal cylinder. Again no scuffing was obtained at 1 kg. At 4 kg, however, scuffing did occur under bone-dry conditions and at oxygen concentrations below 1%. These data are given in Figure 11. Only the combination of high load and hard surfaces, and absence of water and oxygen, brought about this kind of scuffing. The table below summarizes the data.

Ball	Cyl.	Load (kg)	W.S.D. (mm)	Coefficient of Friction
Soft	Soft	1	.34-.38	.09-.07
Hard	Soft	1	.32	.17
Soft	Soft	4	.44	.12
Hard	Soft	4	.41	.12
Hard	Timkin	4	1.63	.46

It again should be mentioned that the Timkin bearing has about twice the roughness of the normal cylinder and that this could also have some effect. At any rate, there are conditions sufficiently severe to bring about scuffing with paraffinic lubes in the absence of water and oxygen.

2. Bone-Dry Conditions Increase Scuffing With Methylnaphthalene

1-Methylnaphthalene and the other condensed ring aromatics show the opposite wear characteristics from the paraffins. These aromatics scuff at extremely low loads at low oxygen and water contents. Bone-dry conditions simply aggravate the situation.

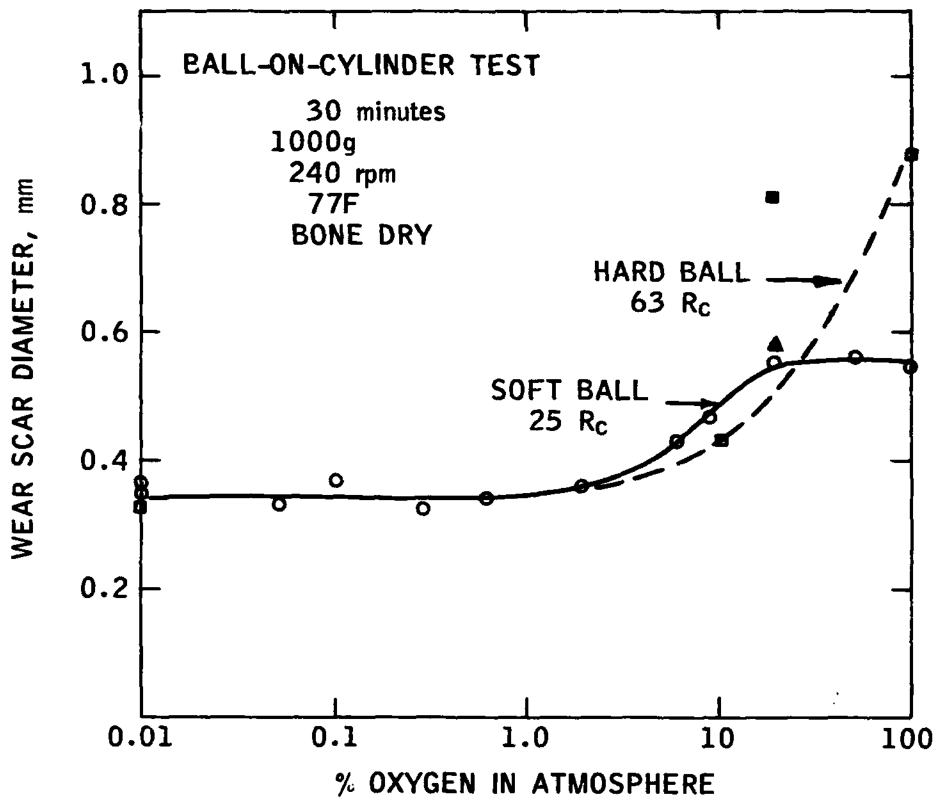


FIGURE 10 - WEAR VS OXYGEN FOR DODECANE - NORMAL HARDNESS CYLINDER

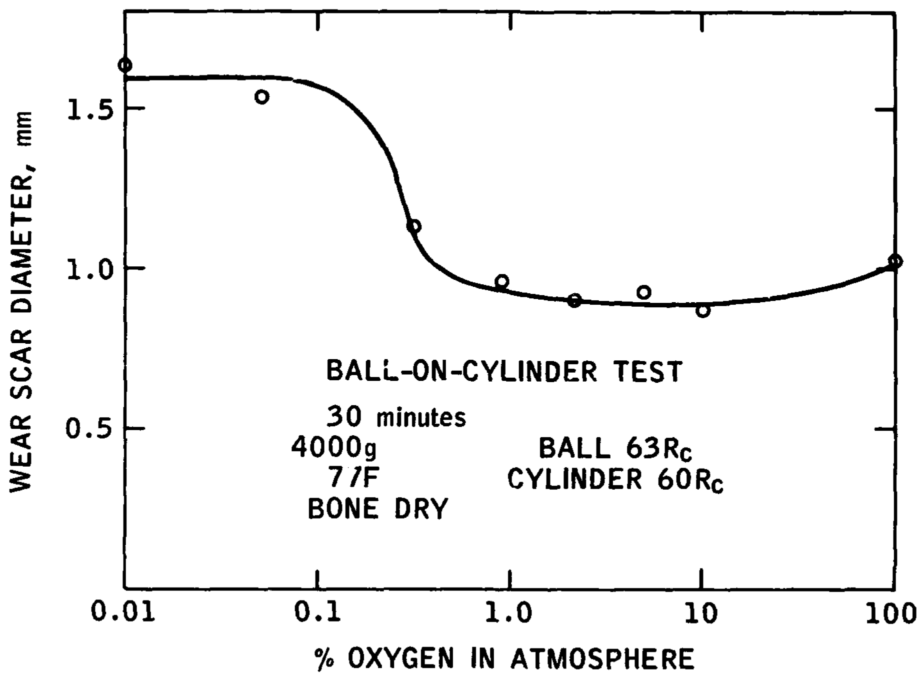


FIGURE 11 - WEAR VS OXYGEN FOR DODECANE - HARD CYLINDER

Figure 12 represents the wear patterns of 1-methylnaphthalene under varying humidities: at bone-dry conditions, at approximately 30 ppm H_2O in the atmosphere, at approximately 500 ppm and at 10,000 ppm. It can be seen that as water concentration increases, the transition percentages of O_2 decrease. This is summarized in the following table:

ppm Water	% O_2 to Prevent Scuffing
0	7
30	4
500	2
10,000	0.01

The data at 30 ppm were those reported earlier. The later data show less of a difference in the final wear scar between scuffing and non-scuffing. The reason for this is unknown, but it does not affect the overall conclusions.

All the above data were taken with a load of 1 kg and the hard ball. An attempted use of the soft balls for this lubricant resulted in no scuffing even under conditions of pure N_2. This is in agreement with the data from the Vickers pump test, where no scuffing was found with methylnaphthalene in nitrogen.

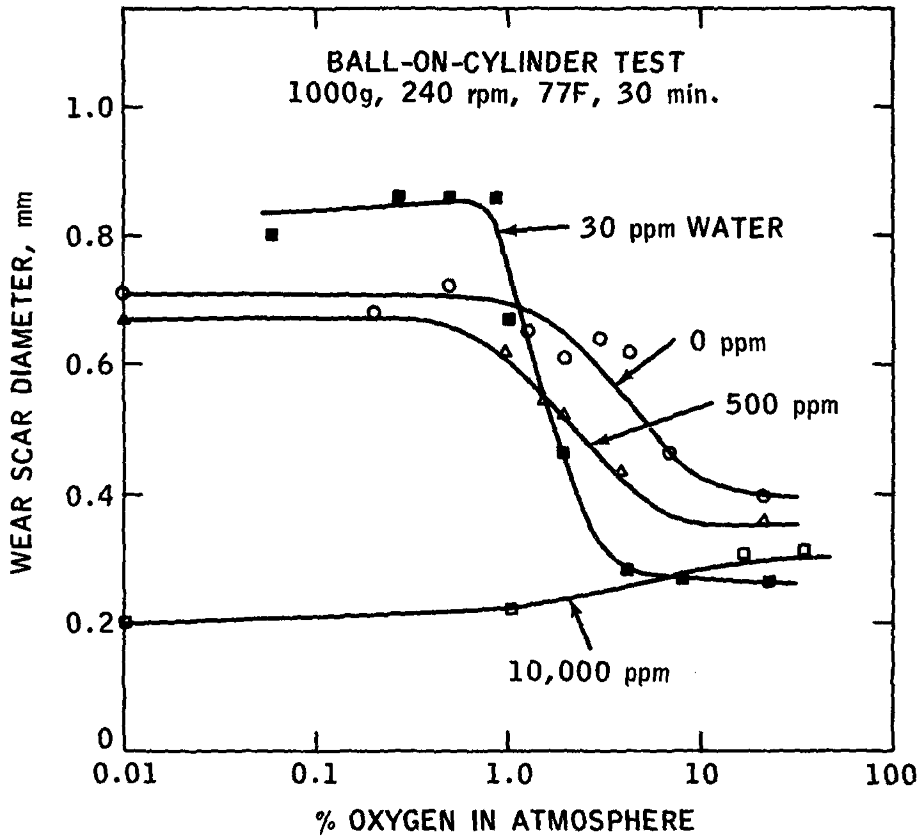


FIGURE 12 - WEAR VS OXYGEN FOR 1-METHYLNAPHTHALENE

IV. FUTURE WORK

The immediate program for the future includes the following items:

- Study of the ability of several aromatic hydrocarbons to prevent scuffing using different metallurgies.
- Determination of effect of iron and iron oxide particles on wear.
- High-temperature scuffing behavior in the four-ball apparatus.
- Two papers are being prepared for publication--one on the advantages of the ball-on-cylinder device for testing jet fuels; the other on the unusual lubricity properties of aromatic hydrocarbons.